Co-Synthesis of Hydrogen and High-Value Carbon Products from Methane Pyrolysis

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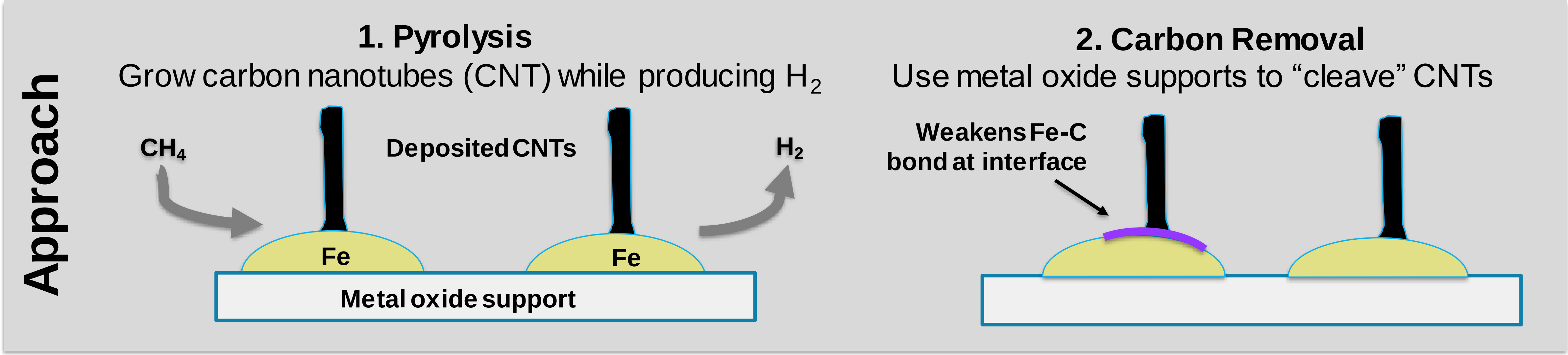
Team Members: Arun Majumdar, Raghubir Gupta

Project Vision

We are developing regenerable catalysts to convert methane into carbon nanotubes and hydrogen without carbon emissions by controlling the reactivity of the carbon-catalyst interface

Total project cost:	$1.47M
Length	24 mo.

The Concept and the Project Objectives



Project Objectives

- Develop a catalytic process for production of H_2 and CNTs – both are important!
- Understand the mechanism of CNT formation and dislodging from the catalyst

Project Targets

- 50% CH_4 conversion with 75% CNT yield
- Long-term cycle testing with >75% activity
- Path to 3 kg CO_2/kg H_2 and **\$1.5/kg H_2**

The Team

Arun Majumdar
expertise in energy generation technologies, heat transfer

Matteo Cargnello
expertise in catalysis, nanostructured materials

Raghubir Gupta
expertise in catalysis, engineering processes, scale-up

Dohyung Kim
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Jimmy Rojas
Grad Student

Eddie Sun
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Sebastian Marin-Quiros
UnderGrad

Vasudev Haribal
Research Process Engineer

J.P. Shen
Senior Chemist

Stanford University

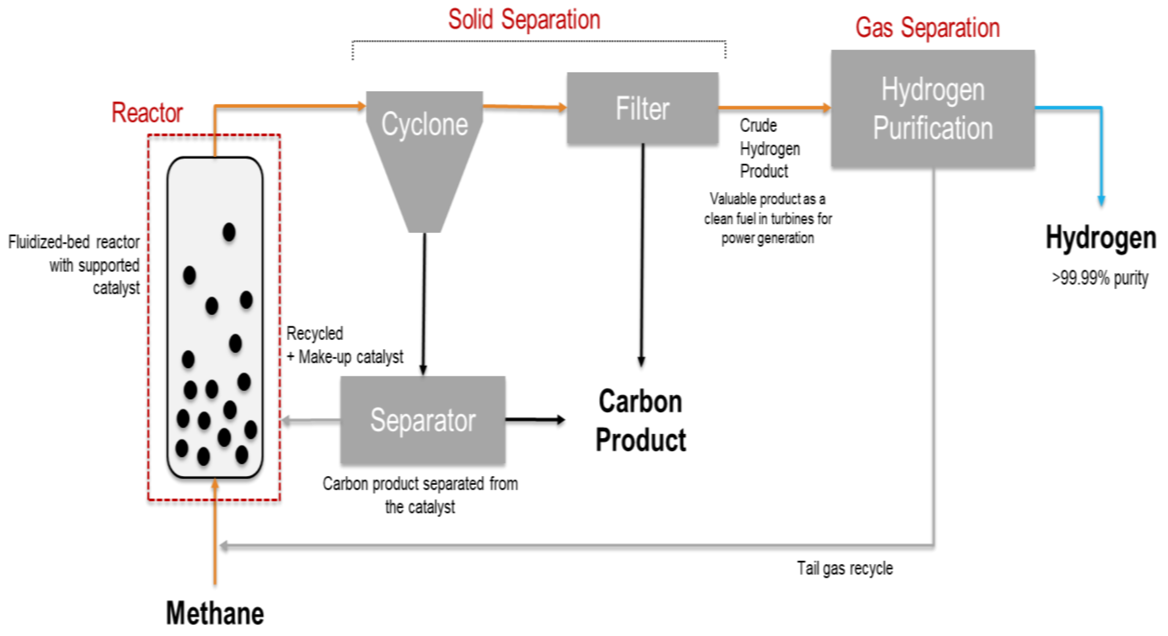
Susteon

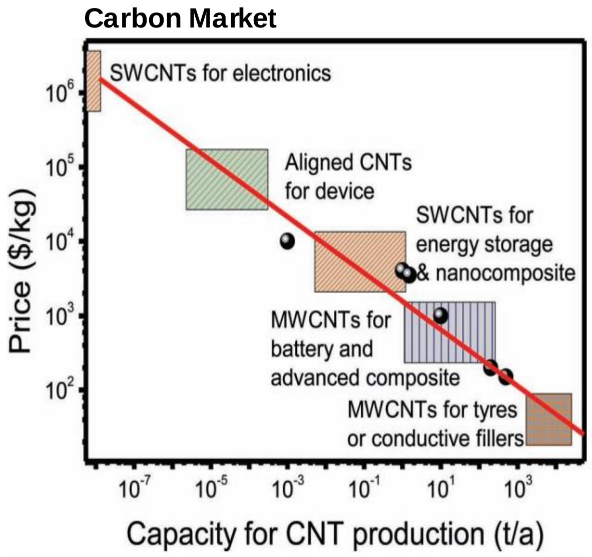
Value Proposition

$CH_{4(g)} \rightarrow C_{(s)} + 2\ H_{2(g)}$
(CNT)

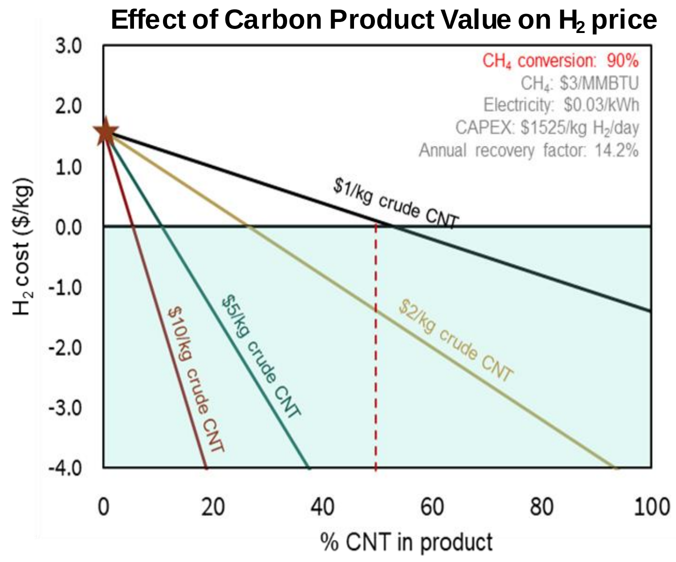
What is our primary product for this technology?

Target is: >50% produced carbon as **CNTs**
through optimization of catalyst, process design, catalyst regeneration and other operating conditions





Zhang et.al., The Road for Nanomaterials Industry: A Review of Carbon Nanotube Production, Post-Treatment, and Bulk Applications for Composites and Energy Storage. *Small, 9(8), 1237–1265.*

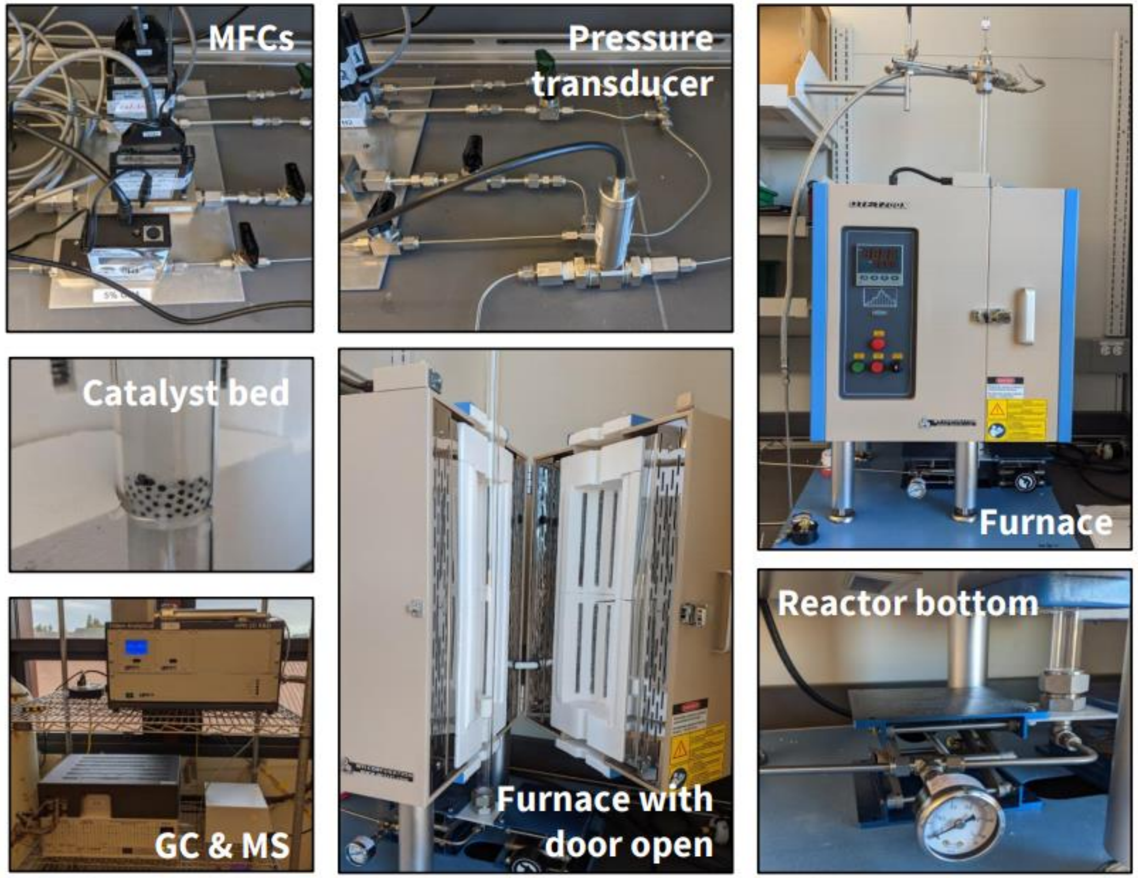


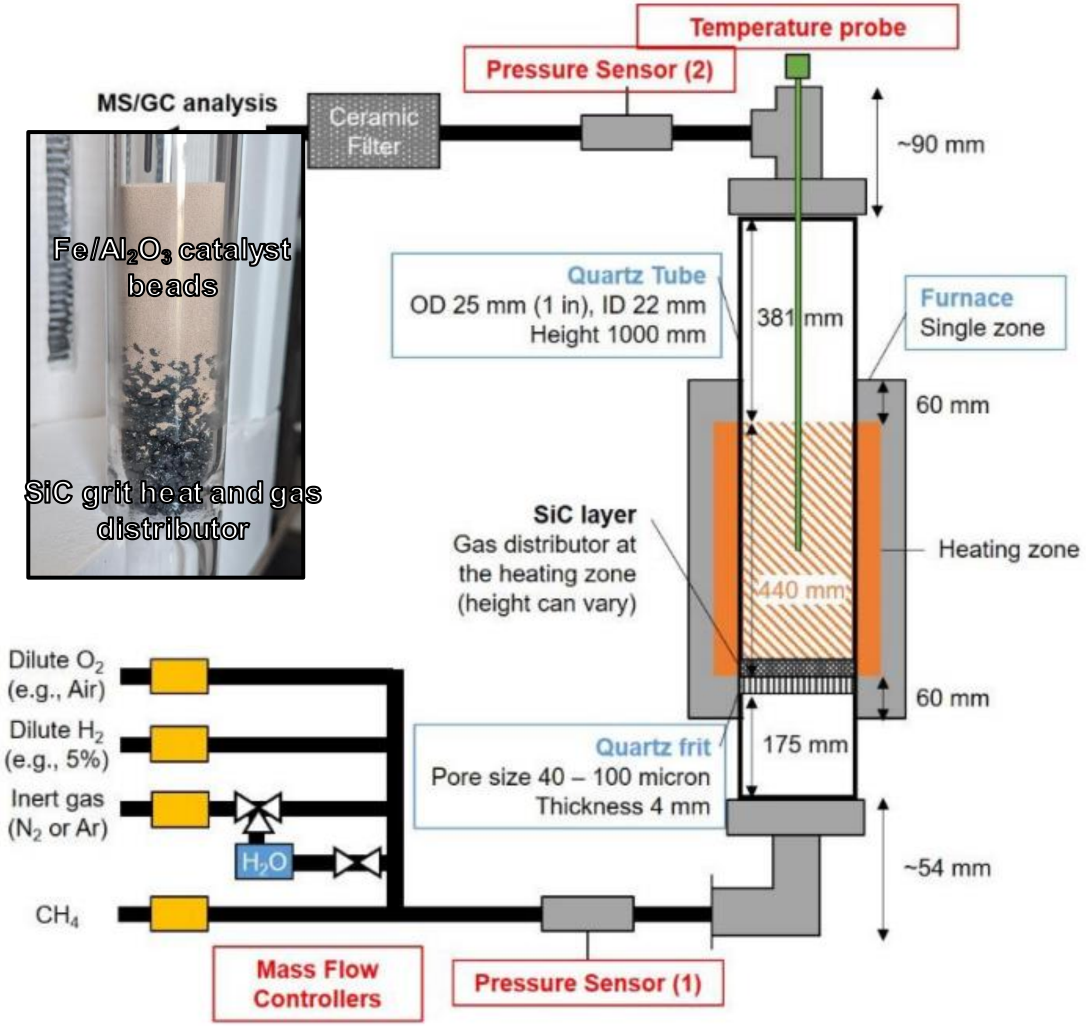
For 10 t H_2 production per day

Price of hydrogen can be lowered by driving production of CNTs

Main Results: Fluidized Bed Process

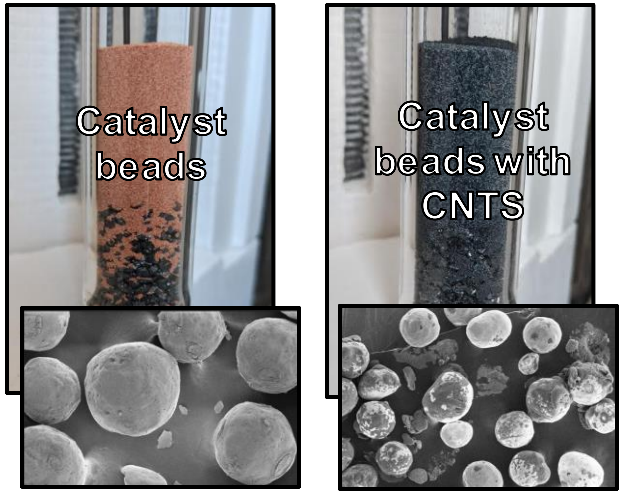
Designed and constructed a bench-scale fluidized bed reactor system for CH_4 pyrolysis

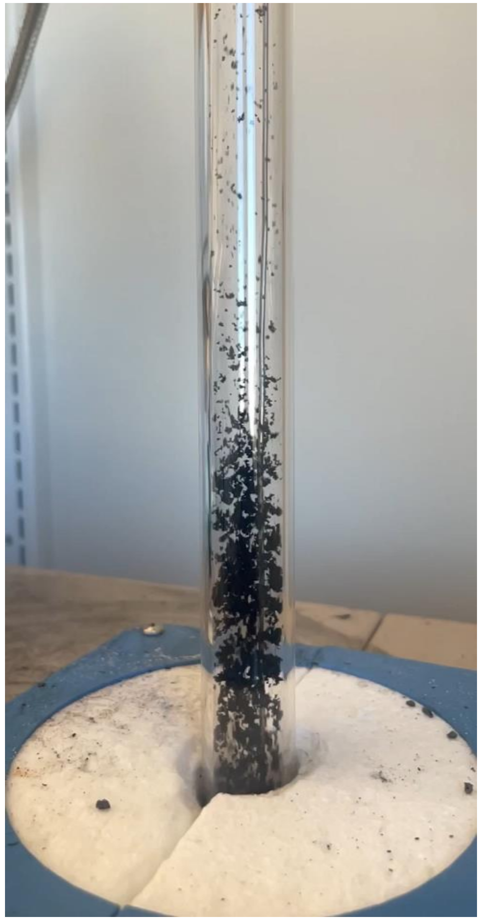




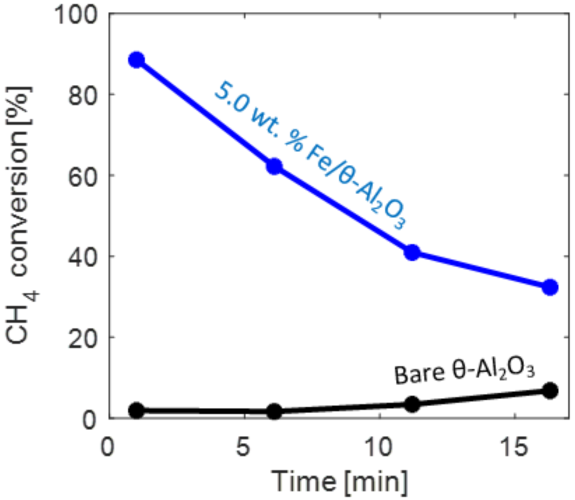
Main Results: Methane Pyrolysis, >99% H_2

Before After

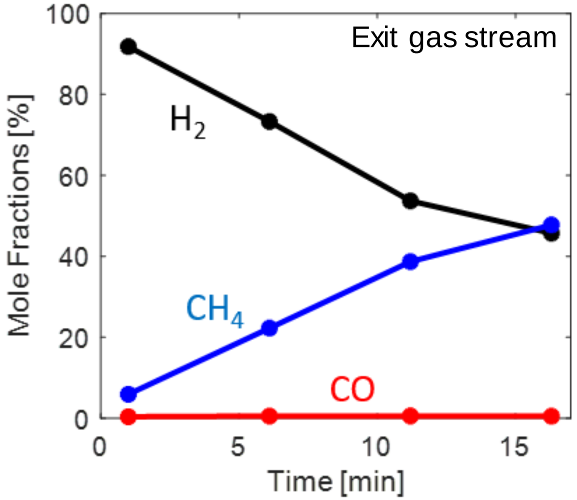




CH_4 pyrolysis activity



Gas product selectivity

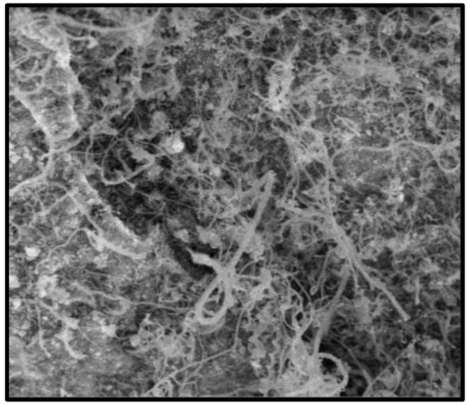


85% CH_4 conversion
(close to thermodynamic equilibrium)
>99% H_2 selectivity
(CO content <1%)
GHSV: 1,221 hr^{-1}

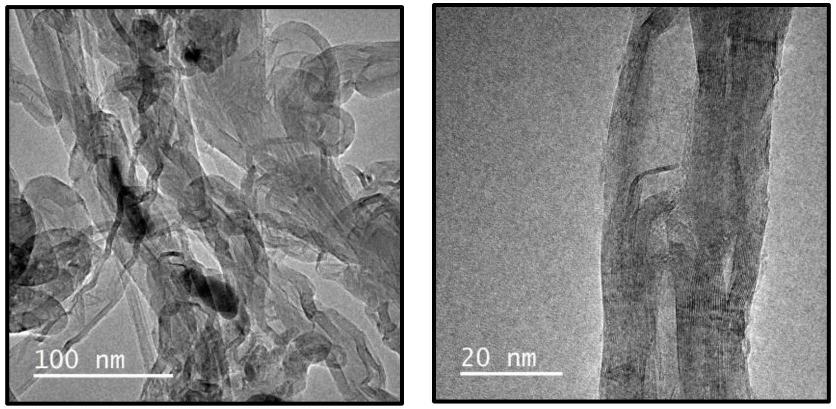
Main Results: Carbon Product

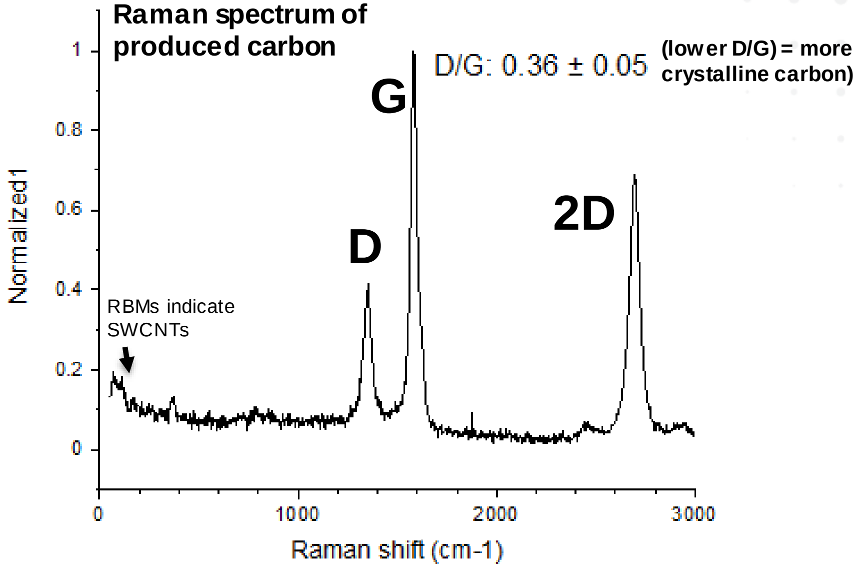
Carbon produced is a mix of single-walled and multi-walled CNTs

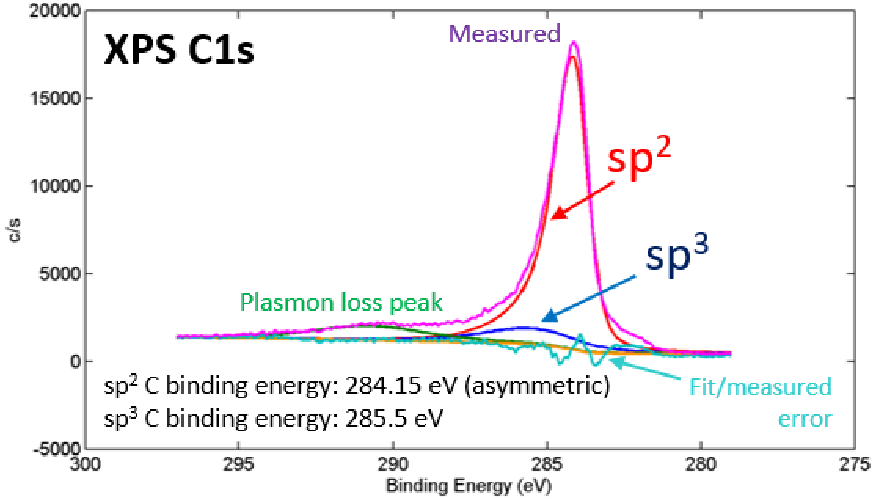
SEM

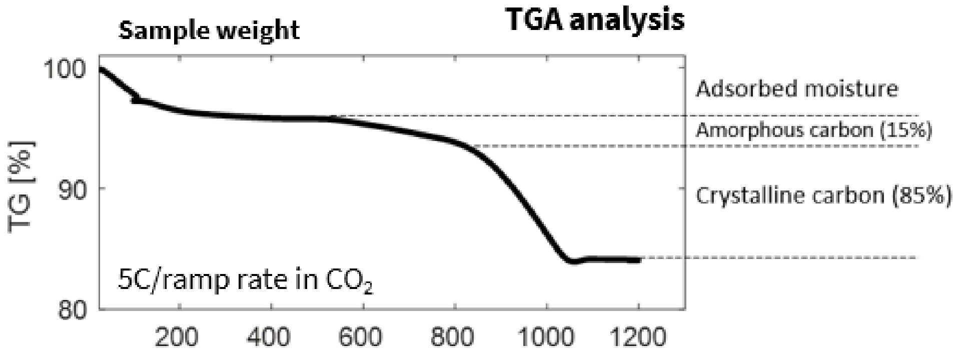


TEM (multi-walled)









>85% of C is CNTs

Main Results: Use of Carbon Product

CNTs made by this process were cast into a CNT film

In collaboration with
Matteo Pasquali, *Rice University*

Only 7 of 27 total commercially-produced CNTs could be spun into fibers
(based on 2017 paper)

Influence of Carbon Nanotube Characteristics on Macroscopic Fiber Properties

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Figure of merit (FOM):
~1000

Figure of merit (FOM) = -Rs ln(T)
Sheet resistance(Rs) and optical transmittance(T)
(state of the art FOM: ~6, lower is better)

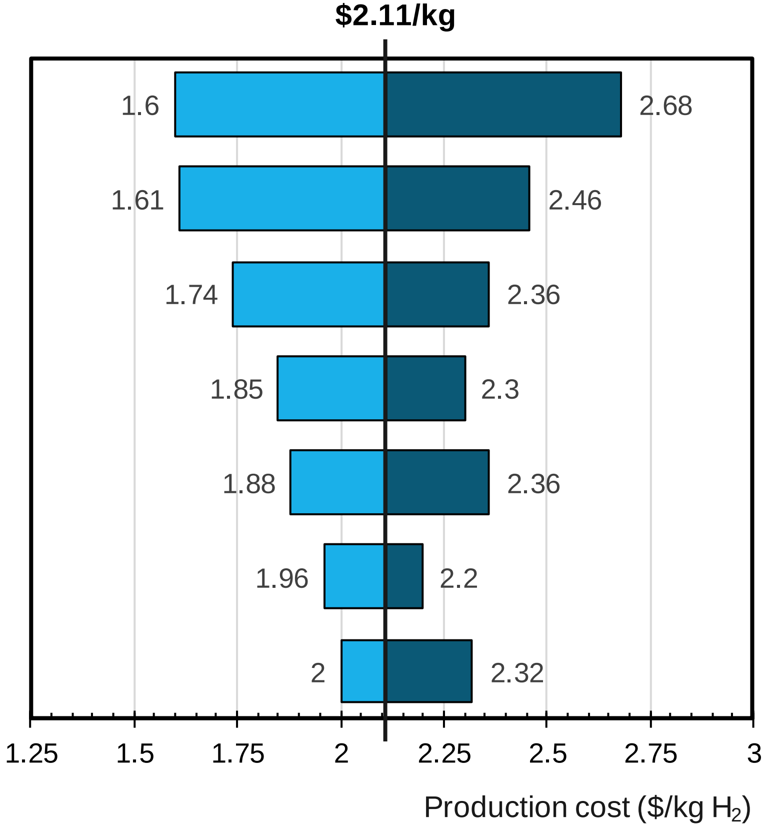
CNT film made by Matteo Pasquali group @ Rice University from our CNTs (after purification)

Main Results: Preliminary TEA

Process Section	Base Capital ($MM)	Contribution	Power ($kWh_e/kg\ H_2$)
Reactor[1]	1.96	20%	
Reactor Heating[2]	1.51	16%	12.0
Carbon Separation[3]	0.16	2%	
Hydrogen Purification[4]	6.00	62%	5.7
Total	**9.64**	**100%**	**17.7**

	10,000 kg/day
Total Capital Investment, $	15,700,000
Total Capital Investment, $/kg/day	1570
Natural Gas Feed, MSCFD	2270
Hydrogen Purity, mol%	99.999
Carbon Production, kg/d	29,950
Production Cost, $/kg H_2	
Capital	0.68
Electricity/Power[5]/Utilities	0.48
Consumables	0.65
O&M	0.30
Total Cost	**2.11**

Sensitivity Analysis



Parameter	Low	Base	High
Natural Gas Conversion (%)	90	25	10
Natural Gas Price ($/MMBTU)	1.0	3.0	5.0
Total Capital ($MM)	10.0	14.8	20.0
Capital Recovery Factor (%)	10.0	14.2	20.0
Electricity Price (¢/kWh)	2.0	3.0	5.0
Catalyst Loading (g/SLM feed)	5.0	10.0	20.0
Power Requirement (kWh/kg)	15.7	17.7	28.3

Even without carbon product credit

This demonstrates the potential to produce H_2 at <$2/kg

[1]Reactor capital: $2MM for 12 m^3 Inconel reactor, req. vol is 1.2 m^3
[2]Heating equipment: $60K for 7kWe
[3]Includes a cyclone and bag filter
[4]H_2 PSA + Compressor: $230,000 for 300 kg H_2/day
[5]Electricity at $0.03/kWh

Challenges and Potential Technical Partnerships

- Biggest challenge is to *effectively regenerate the catalyst* between cycles and *minimize attrition*
- *Effective separation of the catalyst* from the carbon product needs to be achieved
- Study of the carbon-catalyst interface is critical: *in situ* spectroscopy and characterization methods
- **Collaboration with other groups is being explored**
- Risk mitigation: parallel approaches are being pursued with *several supported metal systems*
- *Multi-cycle testing* to demonstrate stability and carbon removal strategies are ongoing